

The Impact Of Arsenic On Coal Fired Power Plants Equipped With SCR – Experience At OUC Stanton

by

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Summary

Arsenic is an especially pernicious catalyst poison. Arsenic can cause physical blocking of active sites by condensation of arsenic in catalyst micropores. Arsenic can also chemically bond to the catalyst surface because As_2O_3 gas reacts readily with O_2 and V_2O_5 on the catalyst surface to form As_2O_5 , deactivating the otherwise active vanadia sites.

Some catalysts are arsenic resistant, which does not mean that they are 100% arsenic proof. An arsenic resistant catalyst will deactivate from exposure to high gaseous arsenic at a much slower and more predictable rate than would occur with a catalyst that is not arsenic resistant.

CaO plays a critical role in mitigating the concentration of gaseous arsenic (As_2O_3) in the boiler. The trace arsenic in the coal oxidizes during combustion to form As_2O_3 gas. If there is adequate free CaO in the gas, most of the As_2O_3 gas reacts with the CaO to form calcium arsenide [$\text{Ca}_3(\text{AsO}_4)_2$], a stable solid material that becomes boiler bottom ash or fly ash. As a result, As_2O_3 gas concentration will be reduced by the presence of CaO .

When fly ash is reinjected, this creates a concentrating mechanism that can increase arsenic concentration by a factor of ten or more.

In European plants where fly ash was reinjected, addition of limestone to the coal was found to mitigate gaseous As_2O_3 levels. Below a threshold, little fixation occurs. However, above the threshold of about 2%-2.5% by weight limestone addition, the gaseous arsenic fixation is very high.

Orlando Utilities Stanton Energy Center Unit #2 is a 468 MW Babcock & Wilcox dry bottom boiler that went into service in June of 1996.

Stanton performed its first air heater wash on unit #2 during the Spring 1997 boiler outage. Catalyst samples were taken and results were received September 1997. Catalyst activity dropped further than anticipated for 8,200 service hours. However, the deviation from expected activity was small - not considered enough for concern at the time.

During the period from spring 1997 through summer 1998, the SCR showed signs of worsening ammonia slip that was not corrected through AIG or control system adjustments.

By September 1998 Siemens had the results of the second catalyst sample tests. Siemens' analysis showed that relative activity dropped below the expected value. And, arsenic concentration on the catalyst surface was found to be 2.71% by weight versus an expected 0.3%. Testing of the archived first outage samples, also found high arsenic at 2.30%.

A coupon test with fresh catalyst coupons was performed in September and October 1998 to verify arsenic poisoning and to estimate the level of gaseous arsenic loading in the SCR reactor. This test showed that arsenic concentrations in the boiler exhaust gas were much higher than expected. However, review of coal analyses for fuels that had been fired showed that coal arsenic levels were well below the expected range of 22.2 ppm to 113.2 ppm.

The coal fired during the September/October 1998 coupon test was analyzed by the fuel department's contract laboratory using ASTM D4606-95. This showed trace arsenic content in the coal of only 0.50 ppm, or about 5 ppm in the ash. Calculations showed that at these low arsenic levels, even if there were no calcium fixation occurring, the gaseous arsenic content would not reach the levels indicated by the coupon test.

A concentrating mechanism was considered as a possible cause, but was ruled out after a thorough mass balance was performed on the plant.

Another set of coal arsenic analyses were performed. A sample of particular interest was of the coal used during the September and October 1998 coupon test. Alabama Power's lab, which used EPA Method 3051 to determine coal arsenic, performed the analysis.¹

All of the tests showed levels below what was expected, but the results of tests using EPA 3051 were well above those of ASTM D4606-95. The coal that was used during the fall 1998 coupon test was analyzed by both ASTM D4606-95 and EPA 3051. For the coal that was fired during the coupon tests, the results showed that EPA 3051 indicated about thirty times more arsenic than was indicated by ASTM D4606.

The gaseous arsenic concentration inferred from the coupon test was compared to the expected gaseous arsenic concentrations based upon the two different coal analysis methods (ASTM D4606-95 and EPA 3051). The results of this analysis suggested that if there is little or no calcium fixation occurring, then the coal arsenic concentration measured by EPA 3051 explains the high arsenic concentration in the unit.

Calcium in the coal was measured. The free CaO was determined to be lower in the coal than expected (about half), raising the likelihood that the cause of the unexpectedly high deactivation rate was due to inadequate free CaO.

Upon a review of test procedures, it was concluded that arsenic was being lost during the sample preparation procedure of ASTM D4606, causing artificially low results. Because EPA 3051 and ASTM D6357 were judged to be more likely to retain arsenic in the sample, these methods are considered superior for measuring arsenic concentration in coal.

Stanton Energy Center has modified its catalyst management plan, while maintaining on the planned three-year addition cycle. Catalyst usage is greater than originally planned.

The implications of this program for other facilities can be summarized as follows:

- The concentration of free CaO in the coal ash is just as important, if not more so, in determining the risk of high arsenic deactivation rates.
- Coal Arsenic concentration should be measured by EPA 3051 or ASTM D6357. Use of ASTM D4606 risks indicating lower coal arsenic than actually exists, which may provide a false sense of security.
- When switching coals or buying on the spot market, coal mineral analyses must be carefully evaluated to assure that arsenic and CaO are in the proper range.
- If any risk of high arsenic conditions are expected due to coal purchasing behavior, boiler operations, or other reasons, then a catalyst formulated for arsenic resistance should be selected.

¹ Alabama Power currently uses ASTM D6357 for analysis of arsenic. This procedure, which was promulgated in January of 2000, was not available at the time of this program. However, ASTM D6357 is similar to EPA 3051.